

*In the Abstract*

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#### **Abstract**

C<sup>4</sup> The sulfur content of liquid cracking products, especially the cracked gasoline, of the catalytic cracking process is reduced by the use of a sulfur reduction catalyst composition comprising a porous molecular sieve which contains a metal in an oxidation state above zero within the interior of the pore structure of the sieve as well as a rare earth component which enhances the cracking activity of the cracking catalyst. The molecular sieve is normally a faujasite such as USY. The primary sulfur reduction component is normally a metal of Period 4 of the Periodic Table, preferably vanadium. The rare earth component preferably includes cerium which enhances the sulfur reduction activity of the catalyst. The sulfur reduction catalyst may be used in the form of a separate particle additive or as a component of an integrated cracking/sulfur reduction catalyst.

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#### **Remarks**

1. This amendment is in response to the Official Action of 25 October 2000 (Paper No. 13). Entry of the amendments set out above is requested. A marked up copy of the amended claims is attached in accordance with the requirements of 37 CFR 1.121(b) and (c).

2.1. The abstract and the specification have been amended in order to identify correctly the period in the Periodic Table that is being referred to in the specification. As filed, the specification stated that the preferred base metals were selected from Period 3 of the Table, with vanadium, iron, cobalt, zinc and gallium being effective and vanadium being the most preferred metal component (page 10, line 28). The reference to Period 3 was intended to cover these metals but was incorrect: these metals belong in Period 4, as shown by the attached references:

"Chemistry of the Elements" Greenwood and Earnshaw, Pergamon Press, 1986.

"Advanced Inorganic Chemistry" Cotton and Wilkinson, John Wiley & Sons, 1980.

Since it is in the public interest to have the specification in scientifically correct form, correction of this error is requested.

2.2. Claims 1 and 9 have been amended to specify that the metal component of the sulfur reduction catalyst is a non-lanthanide. None of the metal components described in the specification are members of the lanthanide series and the change is desirable for this reason alone; in addition, it assists in delimiting the scope of the catalyst from the well-known and established use of rare earths (of the lanthanide series) in zeolitic cracking catalysts. See, for example, Fluid Catalytic Cracking with Zeolite Catalysts, Venuto and Habib, Marcel Dekker Inc., New York 1979, ISBN 0-82470-6870-1, page 32 (copy attached).

3.1. The Examiner has made the restriction requirement final, stating that applicants have not provided sufficient reasons why the proposed alternate use cannot be accomplished. It is assumed that the proposed alternate use is the process referred to without further elaboration in Paper No. 11 as an "ion sieve process".

3.2. With respect, the Examiner has misplaced the burden of proof in this case. It is not incumbent on the Applicant to provide evidence in support of a proposition (that the claims are directed to the same invention) but rather, the Examiner, who is required to support agency action by substantial evidence made of record in the proceedings. The Patent and Trademark Office is an "agency" subject to the constraints of the Administrative Procedure Act (APA), as established by the Supreme Court decision in *In re Zurko*, 50 USPQ 2d 1930. Here, the conclusion that the claims are directed to separate and different inventions, with its consequent refusal to examine them (and potentially, the imposition of a further and separate application in order to obtain a patent for the claims in question) constitutes "agency action" and a reviewing court would apply the APA's court/agency review standards in the absence of any exception (and there is no exception). The Examiner's action is therefore subject to the requirements of the Act which include the requirement that the action be supported by substantial evidence.

Under the APA the agency decision in this case would be subject to judicial review under Section 706 which sets out the standards that govern the scope of court "review" of agency action. Section 706 (originally enacted in 1946) states that a reviewing court shall--

"(2) hold unlawful and set aside agency . . . findings . . . found to be --

(E) *unsupported by substantial evidence* in a case subject to sections 556 and 557 of this title or *otherwise reviewed on the record of an agency hearing provided by statute*; . . ."  
(Emphasis added)

3.3. Adherence to the regulatory prescription must therefore be determined by the evidence of record rather than on the mere assertion. Here, there is no substantial evidence in the present record which shows that the claimed catalysts can be used in any different process. There is certainly no evidence that the claimed catalysts can be used in the so-called "ion sieve" process. The Examiner's word is not evidence; it does not create fact. There is, therefore, nothing to warrant the Examiner's speculation and no credible - or, even, any - evidence to support the Examiner's restriction requirement. The requirement should therefore be withdrawn. To reiterate this fundamental requirement of the APA: it is not for the Applicant to support a case of the unitary character of the invention by adducing evidence to this effect but rather, the Examiner who is given the burden by the APA, of supporting the agency action by substantial evidence.

3.4. Consistent with the provisional election, applicants maintain the election of Group 1, claims 1-12 drawn to the process. Applicants reserve their rights with respect to the claims of Group 2 as well as their right with respect to contest this restriction requirement further. Consistent with this reservation, the nonelective claims are not cancelled at the present time.

4.1 The Examiner has rejected claims 1-3, 5, 6 and 8 under 35 USC 102(b) as anticipated by Beck U.S. 4,588,702.

4.2. Beck discloses a catalytic cracking process for hydrocarbon feeds which may contain polar compounds such as sulfur substituted hydrocarbons (column 14, lines 13-

14. According to the Beck patent, the catalyst which is to be used for the production of gasoline by the catalytic cracking process may include a number of different components including a large pore (Y-type) zeolite, a clay, an acidic silica-alumina co-gel matrix, alumina and, as metal components, from 0.1 to 3 wt% (claim 1, column 35, lines 10-12), generally 0.5 to 2.0 wt% (column 18, line 50-51) of rare earths comprising lanthanum and cerium. It is stated that the rare earths are partially exchanged onto the zeolite from solution, with the zeolite being contained in the acidic matrix (silica-alumina co-gel) with a portion of the rare earth precipitated into the matrix (column 35, lines 15-19). The specification states that the deposition or precipitation of lanthanum in the matrix - as compared with ion exchange - is able to reduce the deleterious effect of vanadium (column, 21, lines 41 - 47), implying that deposition or precipitation is to be favored over ion exchange for the lanthanum component.

4.3. The Examiner has concluded that Beck discloses a cracking process with steps and catalyst components corresponding to those claimed by applicants. See Paper No. 13, page 4. The Examiner concedes that the reference does not refer to a reduction in the sulfur concentration of the feed (correctly stated, this would be a reduction in the total sulfur concentration of the liquid products since the sulfur content of the feed remains what it is) but the Examiner considers the sulfur reduction to be an inherent feature of the process because, it is asserted, the reference discloses the same process steps/catalyst claimed by applicants (Paper No. 13, page 4) and the desulfurization would "obviously have been provided as a result of the operation " of the Beck process.

4.4. Applicants do not concede that the Beck patent anticipates the claims in question because there is nothing in Beck which indicates that the vanadium enters the Beck catalyst to become present in the interior pore structure of the molecular sieve in an oxidation state greater than zero. (Applicant's attorney apologizes for confusing the issue in the previous Amendment by taking up the question of the oxidation state of the rare earth; the oxidation state of the rare earth component has not been stated in the claims and is therefore not at issue in these proceedings). When the rare earth is exchanged onto the zeolite of the Beck catalysts for an aqueous solution, as described in Beck column 31, lines 64-65), it will be present in the form of cations which have undergone exchange with the hydrogen or other cations (e.g.  $\text{Na}^+$ ) on the zeolite, the

rare earth is therefore in an oxidation state greater than zero within the pore structure of the zeolite at least at the time of exchange onto the zeolite.

4.5. Beck does not, however, disclose the use of the non-lanthanide transition metals as the first metal component of the presently claimed catalysts; these metals are used in addition to the rare earth component. Specifically, there is nothing in Beck which teaches use of the metals vanadium, iron, cobalt or zinc within the interior pore structure of the molecular sieve component of the Beck catalyst, with these metals being in an oxidation state greater than zero.

4.6. In dealing with the question of the cations which may be on the metal, the Examiner has correctly pointed out that the Beck catalysts contain lanthanum and/or cerium (Paper No. 13, page 3, bottom), but has not utilized Beck beyond its teachings of rare earths in the catalyst. The present catalysts are, however, defined as containing two metal (cation) components, one of which is a rare earth and the other is not. Beck does not teach catalysts of this type nor their use in catalytic cracking. Beck does indicate, as noted by the Examiner, that the vanadium is to be immobilized. If this suggestion is taken *ex hypothesi* in the light proposed by the Examiner, that the vanadium is immobilized in the *catalyst* (Paper No. 13, page 11), it still does not indicate that the vanadium enters the *interior pore structure of the zeolite* there to remain in an oxidation state greater than zero. The catalyst of Beck as well as that of the present invention, includes both a matrix material (or binder) as well as the sieve component and it is perfectly consistent with Beck's objective of immobilizing the vanadium, that this poison should be immobilized in the matrix rather than by incorporation into the zeolite. In fact, if vanadium from hydrocarbon feeds is (as was known to be) deleterious to the zeolite it might well seem better sense to immobilize it in the matrix rather than to seek to get it into the sieve. As to the trapping of the vanadium in the pores of the catalyst (Beck column 8, lines 63-66; Paper No. 13, page 12), the actual teachings of the reference do not seem to support the Examiner's views. Beck, in this passage, refers to the metal passivator or immobilizer being incorporated into the matrix (lines 60-61), a technique involving *inter alia*, "the precipitation of lanthanum *into the matrix* to immobilize vanadia" (column 8, lines 63-64, emphasis added). Thus, the reference appears to directly contradict the Examiner's position: it teaches that the rare earth is incorporated into the *matrix*, there to immobilize the vanadium. This means that the vanadium enters

the *matrix* and stays there, that it does not enter the sieve component of the catalyst. The Examiner's comment that since the (Beck) process is operated with vanadia trapped in the pores it is considered to read on applicant's catalyst containing vanadium in the pores (Paper No. 13, page 12) is warranted by Beck only to the extent that the pores in question are the pores of the *matrix*, where the vanadium is immobilized by the lanthanum (column 8, lines 61-66). To imply that Beck either discloses or suggests that the vanadium is in the pores of the sieve component is unwarranted fancy.

4.7. Thus, the catalysts described in Beck are not the same as those used in the present invention and therefore there is no reason to suppose that any reduction in product sulfur would have taken place in the Beck process. The rejection under 35 USC 102(a) based on the Beck patent is therefore unjustified and should be withdrawn. The same holds true for the rejection under 35 USC 103 since there is nothing in Beck which indicates the desirability of using the combined cationic components which are characteristic of the present catalytic materials.

5.1. Claim 4 has been rejected under 35 USC 103(a) as unpatentable over Beck in view of Kugler, U.S. 4,944,864.

5.2. Kugler is concerned with a fluid catalytic cracking process and especially with a method of using the catalyst on hydrocarbons, which contain one or more soluble metal poisons including vanadium, nickel or iron (column 1, lines 13-15). The Kugler catalyst contains one or more water-insoluble strontium compounds in addition to the zeolite and the catalyst matrix which are intended to react with and trap the metal poison so as to preserve the structure of the zeolite and, in addition, lower the coke and hydrogen production during the process (column 1, lines 19-22).

5.3. The Examiner has conceded that a difference is noted between the Beck reference and applicant's claimed invention in that Beck does not disclose the use of a vanadium containing catalyst (Paper No. 13, page 5). The Examiner refers, however, to Kugler to show that it is "known in the art that vanadium contaminants in a hydrocarbon feed which remain on the catalyst during regeneration are oxidized and that the oxidized vanadium compounds become mobile and react with the zeolite components of the catalyst" From this the conclusion is that the regenerated catalyst contains vanadium



(Paper No. 13, page 5). The Examiner then infers that it would have been obvious to one of ordinary skill in the art to utilize a vanadium containing catalyst because the reference of Kugler teaches that it is known in the art that regenerated catalyst recycled for further cracking would contain vanadium components (Paper No. 13, page 6). Not only does this assertion ignore a specific and characteristic feature of the claims, it is also inconsistent with the state of knowledge in the art and with any reasonable interpretation of the Kugler reference which might be drawn by a person of skill in the art of catalytic cracking.

5.4. First, the present claims require that the first metal component should be present within the interior pore structure of the molecular sieve and that it should be present in an oxidation state greater than zero. See claims 1 and 9. Kugler, either alone or read in the light of Beck, does not disclose this feature, far less suggest its desirability. There is therefore nothing in the combined Beck and Kugler teachings which as a matter of words points towards the present invention.

5.5. Neither Beck nor Kugler states that the vanadium enters the pore structure of the zeolite. The following portion from Kugler is of particular note:

"[T]he heavier crudes contain substantially more organic metal compounds, such as vanadium and nickel porphyrins. These metals cause many undesirable reactions in heavy oil cracking catalysts in that the metals, specifically nickel and vanadium, are quite harmful to the fluidized cracking catalysts used. These metals, present in the high-boiling fractions, deposit on cracking catalyst and accumulate with time. They act as poisons and have the resulting effect of increasing undesirable hydrogen and coke yields and as well as decreasing the selectivity of the catalyst in making liquid products. Recently, vanadium has been found not only to increase hydrogen and coke yields but also to attack the zeolite itself, the high activity component of a catalytic cracking catalyst. See, Ritter et al, "A Look at New FCC Catalysts for Resid", Oil and Gas J., July 6, 1981, pg. 103. The mode of vanadium attack is not understood; however, available data indicate that *vanadium can migrate through the catalyst particle and accumulate in areas of high zeolite concentration*". [Emphasis added].

From this passage it is clear that the presence of vanadium in the feeds which are processed in the FCCU is considered highly undesirable: the vanadium acts as a poison which degrades the structure of the zeolite and diminishes the high activity of

the zeolite component of the catalyst. Note that Kugler refers to the migration of the vanadium through the catalyst particle to areas of high zeolite concentration (column 1, lines 54-58) where, the zeolite being susceptible to vanadium attack (column 1, lines 59-60) is directly attacked (column 1, line 51). But this is all Kugler has to say about the final destination of the vanadium in the catalyst: it accumulates in areas of high zeolite concentration. This does not say that the vanadium enters the pore structure of the zeolite nor that it will be - wherever located - in an oxidation state greater than zero.

Kugler notes that the past practice has been either to avoid charging high boiling point feedstocks (since the vanadium containing porphyrins are concentrated in the high boiling fractions) or limiting total metal concentrations to a low level (column 1, lines 63-66). The use of various passivation procedures has been also proposed but what is clear overall, is vanadium is considered a highly undesirable factor in the fluid catalytic cracking process. This is supported by the Wormsbecher article referred to on page 12 of the specification, of record.

5.4. The Beck reference is also instructive in this respect. Beck notes that "a second reason for the high pore volume is due to the high metals e.g. nickel, *vanadium* and iron, contained in the feeds utilized with the present invention which can gradually build up *on the outer surface of the catalyst*, decreasing pore volume and blocking off the acidic matrix from contact with fresh feed materials". (Beck, column 19, lines 25-30, emphasis added). Thus, Beck recognizes that vanadium has an undesirable effect on the catalyst as a whole from its location *on the outer surface of the catalyst*. This clearly means that the vanadium picked up from the hydrocarbon feeds accumulates on the outside of the *catalyst* (not even the outside of the zeolite crystals but rather, the outside of the *catalyst* as a whole). Equally clearly this means that the vanadium is not in the interior pore structure of the zeolite. Thus, even if Beck were to indicate that the presence of the vanadium were in some manner desirable, there would be no disclosure or suggestion that the vanadium should be located within the interior pore structure of the zeolite, as claimed in the present application.

5.5. The different locations of the vanadium in the prior art materials as compared to that of the present invention is no accident and should come as no surprise. The present invention deliberately incorporates vanadium into the catalyst, into the pore



structure of the molecular sieve (zeolite) component and it does this during the manufacture of the catalyst using vanadium compounds and techniques adapted to this end. Beck and Kugler, by contrast, do not attempt to incorporate vanadium into the catalyst but accept the inevitable, that it will become attached to the catalyst during use. The vanadium in this case comes from the hydrocarbon feed and is clearly not in a form which is apt to be incorporated into the zeolite, as noted by both Beck and Kugler. Nor is the manner of use of the catalysts apt to incorporate the vanadium into the zeolite pore structure: no provisions for impregnation nor exchange are made or intended, not unnaturally since vanadium was considered by Beck, Kugler and many others to be very undesirable in its pernicious effects on cracking catalysts.

5.6. Given, therefore, the strong antipathy to the presence of vanadium in the FCC process, it stretches the imagination why a person of ordinary or, indeed, any degree of skill in the art would have considered it rationally desirable and therefore obvious, to incorporate vanadium deliberately into a catalyst to be used in the process. The logic of the thing is that a person skilled in the fluid catalytic cracking art would have considered it very *undesirable* to have vanadium present at all in the catalyst, and with greater reason, on the zeolite component of the catalyst. To put vanadium directly on or even in the zeolite component where it would have been expected to have a poisonous, destructive effect on the zeolite structure and on catalytic activity, flies in the face of reason. Certainly, there is no reason apparent on the face of the art of record why any incentive to add vanadium to a catalytic cracking catalyst might exist.

5.7. Since obviousness is, as noted above, to be properly measured by desirability not mere possibility, it is submitted that the Examiner's inference is incorrect: it would not have been obvious to one of ordinary skill in the art to utilize a vanadium-containing catalyst even in view of the fact that catalysts recycled for further cracking may contain vanadium components picked up from the cracking feed. In fact, the presence of the vanadium was *undesirable* and a person skilled in the art would not have sought to incorporate vanadium directly into the catalyst at all, far less into the "interior pore structure of the molecular sieve" (*cf.* Claims 1 and 9) as this component was thought to be directly subject to attack by the vanadium which a consequent diminution of catalytic structure and activity. The discovery that vanadium could be usefully incorporated into the present catalyst with a desirable catalytic effect (sulfur reduction) without significant

deterioration of catalytic activity was totally unexpected. Clearly, the manner of incorporation of the vanadium into the catalyst is a significant feature of the present invention and this is neither disclosed nor made obvious by the disclosure in Kugler or any other reference of record. Reconsideration of this rejection is therefore in order.

6.1. Claim 7 has been rejected under 35 USC 103(a) as unpatentable over Beck in view of Tan-no, U.S. 5,646,082 and Kugler. The Examiner has noted that several differences are noted between the reference of Beck and the claimed invention, including the specific UCS, the silica:alumina ratio of the USY composition and the use of the vanadium component (office action, page 7).

6.2. The Tan-no reference has been cited to show that it is conventional in the FCC art to crack a feed in the presence of a USY containing catalyst, with a rare earth component and a UCS in the range of 24.45 to 24.55Å (2.445-2.455 nm) and a silica:alumina ratio of 5-11. While the factual teachings of Tan-no as set out in U.S. 5,646,082 are conceded, with the notation that Tan-no refers to the zeolite not as a USY zeolite, as suggested by the Examiner (office action, page 7) but rather, as a stabilized zeolite Y of improved stability obtained by hydrothermal treatment and optional treatment with mineral acid and other materials (column 3, lines 46-54) and a specific heat shock treatment (column 4, lines 28-58). More importantly than this, however, the combination of references cited against claim 7 does not indicate the obviousness of using a vanadium component in the catalyst with this component located within the interior pore structure of the sieve component. As pointed out in Section 5 above, it would not have been obvious to one of ordinary skill in the art to use vanadium in an FCC catalyst at all because of its undesirable effects both upon the catalyst as a whole (see Beck) and specifically, the sieve (zeolite) component of the catalyst (see Kugler). Applicant therefore rejects the suggestion that it would have been obvious to utilize a vanadium containing catalyst because of Kugler's teaching regarding the presence of vanadium components in the FCC process. Reconsideration and withdrawal of the rejection of claim 7 is therefore required.

7.1. Claims 9-12 have been rejected under 35 USC 103(a) as unpatentable over Beck in view of Occelli, U.S. 4,615,996. The Occelli reference is relied on to support the proposition that is conventional in the art to use FCC catalysts with particle sizes

less than 75 microns. This much may be conceded although it is pointed out that the passages cited by the Examiner do not appear to support the proposition. A more relevant portion of the Occelli reference would be the passage at column 7, lines 59-67.

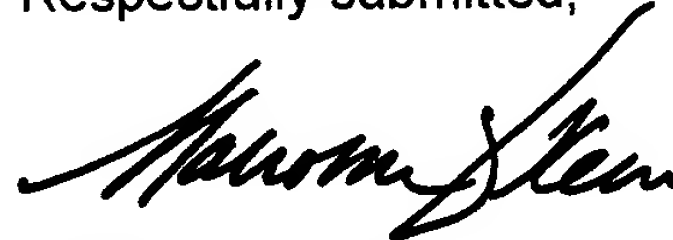
7.2. With respect to the substantive merits of this rejection, the comments set out above with respect to the Beck reference are reiterated. There is nothing in Beck which indicates the desirability and therefore the obviousness of using a catalyst which contains a first metal component within the interior pore structure of the molecular sieve in an oxidation state greater than zero in combination with rare earth within the interior pore structure of the sieve. More specifically, there is nothing in Beck which indicates the obviousness of using vanadium or zinc as the first metal component and rare earth cations as the second metal component. In addition, as noted above, the use of vanadium would have been considered highly undesirable in the art, especially when specifically combined with the zeolite component of the catalyst. This rejection should therefore be withdrawn, especially with regard to claim 11.

8.1. The final rejection made by the Examiner is a double-patenting rejection based on co-pending application Serial No. 09/221,540 (Mobil Case 10102-1) making this rejection provisional in character. Applicant does not concede the correctness of this rejection for the reasons set out in the previous response. As previously noted, there is a difference in catalytic activity between the catalyst which contains cerium as the rare earth component on the one hand, and catalysts which contain rare earth mixtures, on the other (specification page 23, lines 16-24). Among the rare earth ions, cerium exhibits a unique property in that the cerium/vanadium/USY catalyst exhibits higher cracking activity but also exhibit increased gasoline sulfur reduction activity in the FCC process. This difference in catalytic activity is unexpected (at least, as far as indicated by any reference of record) and because of this, the cerium containing catalysts of the cited application are considered to be patently distinct from those of the present application. The fact that the present claims may refer to the presence of cerium in combination with lanthanum does not affect the fact that cerium, when it is substantially the sole rare earth component, exhibits a superior relative performance. Given that this difference in performance exists, it is difficult to see how the Examiner's assertion that it would have been obvious to select "any second metal amount overlapping the amount claimed" (in the copending application) can be objectively justified. Again, the

Examiner has failed to consider that the invention resides not only in the materials and amounts in which they are used but their inherent properties, all of which are to be considered in any assessment of obviousness and obviousness type double patenting. Applicants reiterate their submission that the difference in catalytic activity between the cerium and the other rare earths is unexpected and could not have been predicted by a person of skill in this art. On this basis, it is submitted that there is no double patenting between the present application and the cited application and for this reason the double-patenting rejection should be withdrawn.

9. In view of the amendments and remarks set out above, allowance of the application is requested.

Respectfully submitted,



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We claim:

1. A method of reducing the sulfur content of a catalytically cracked petroleum fraction, which comprises catalytically cracking a petroleum feed fraction containing organosulfur compounds at elevated temperature in the presence of a cracking catalyst and a product sulfur reduction catalyst which comprises a porous molecular sieve having (i) a first metal component which is within the interior pore structure of the molecular sieve and which comprises a non-lanthanide base metal in an oxidation state greater than zero and (ii) a second metal component which is within the interior pore structure of the molecular sieve and which comprises at least one rare earth, to produce liquid cracking products of reduced sulfur content.
2. A method according to claim 1 in which the product sulfur reduction catalyst comprises a large pore size or intermediate pore size zeolite as the molecular sieve component and, as the first metal component, at least one metal of Period 34, Groups 5, 8, 9 or 12 of the Periodic Table.
3. A method according to claim 2 in which the large pore size zeolite comprises zeolite USY.
4. A method according to claim 2 in which the first metal component comprises vanadium.
5. A method according to claim 2 in which the second metal component comprises lanthanum alone or in combination with cerium.
6. A method according to claim 1 in which the second metal component is present in an amount from 1 to 10 weight percent of the catalytic composition.
7. A method according to claim 1 in which the product sulfur reduction catalyst comprises a USY zeolite having a UCS of from 2.420 to 2.455 nm, a bulk silica:alumina ratio of at least 5.0 as the molecular sieve component and, as the first metal component, at least one of zinc or vanadium in an oxidation state greater than zero and, as the second metal component, a combination of lanthanum and cerium.

8. A method according to claim 1 in which the sulfur reduction catalyst is a separate particle additive catalyst.

9. In a fluid catalytic cracking process in which a heavy hydrocarbon feed comprising organosulfur compounds is catalytically cracked to lighter products by contact in a cyclic catalyst recirculation cracking process with a circulating fluidizable catalytic cracking catalyst inventory consisting of particles having a size ranging from about 20 to about 100 microns, comprising:

(i) catalytically cracking the feed in a catalytic cracking zone operating at catalytic cracking conditions by contacting feed with a source of regenerated cracking catalyst to produce a cracking zone effluent comprising cracked products and spent catalyst containing coke and strippable hydrocarbons;

(ii) discharging and separating the effluent mixture into a cracked product rich vapor phase and a solids rich phase comprising spent catalyst;

(iii) removing the vapor phase as a product and fractionating the vapor to form liquid cracking products including gasoline,

(iv) stripping the solids rich spent catalyst phase to remove occluded hydrocarbons from the catalyst,

(v) transporting stripped catalyst from the stripper to a catalyst regenerator;

(vi) regenerating stripped catalyst by contact with oxygen containing gas to produce regenerated catalyst; and

(vii) recycling the regenerated catalyst to the cracking zone to contact further quantities of heavy hydrocarbon feed,

the improvement which comprises

reducing the sulfur content of a the gasoline portion of the liquid cracking products, by catalytically cracking the feed fraction at elevated temperature in the presence of a product sulfur reduction catalyst which comprises a porous molecular sieve having (i) a first metal component which is within the interior pore structure of the molecular sieve and which comprises a non-lanthanide base metal in an oxidation state greater than zero and (ii) a second metal component which is within the interior pore structure of the molecular sieve and which comprises at least one rare earth.



10. A method according to claim 11 in which the cracking catalyst comprises a matrixed faujasite zeolite.

11. A method according to claim 12 in which the product sulfur reduction catalyst comprises a large pore size or intermediate pore size zeolite as the molecular sieve component, vanadium as the first metal component and a combination of cerium and at least one other rare earth metal as the second metal component.

12. A method according to claim 13 in which the large pore size zeolite of the product sulfur reduction catalyst comprises zeolite USY.

13. A fluidizable catalytic cracking product sulfur reduction catalyst composition for reducing the sulfur content of a catalytically cracked gasoline fraction during the catalytic cracking process, which comprises fluidizable particles having a size ranging from about 20 to about 100 microns of (i) a porous molecular sieve component, (ii) a first metal component comprising a non-lanthanide base metal in an oxidation state greater than zero located within the interior pore structure of the porous molecular sieve component and (ii) a second metal component comprising a rare earth metal located within the interior pore structure of the porous molecular sieve component.

14. A fluidizable catalytic cracking product sulfur reduction catalyst composition according to claim 13 in which the porous molecular sieve component comprises a porous hydrocarbon cracking sieve component.

15. A fluidizable catalytic cracking product sulfur reduction catalyst composition according to claim 14 in which the porous molecular sieve component comprises zeolite USY having a UCS of from 2.420 to 2.455 nm and a bulk silica:alumina ratio of at least 5.0.

16. A fluidizable catalytic cracking product sulfur reduction catalyst composition according to claim 15 in which the porous molecular sieve component comprises zeolite USY having a UCS of from 2.420 to 2.435 nm and a bulk silica:alumina ratio of at least 5.0.

17. A fluidizable catalytic cracking product sulfur reduction catalyst composition according to claim 13 which contains from 0.2 to 5 weight percent vanadium as the first metal component, based on the weight of the zeolite, of the first metal component.

18. A fluidizable catalytic cracking product sulfur reduction catalyst composition according to claim 13 which comprises as the second metal component, a combination of cerium and at least one other rare earth.

19. A fluidizable catalytic cracking product sulfur reduction catalyst composition according to claim 13 in which the metal components have been introduced into the zeolite as exchanged cationic species within the zeolite pores.

20. A fluidizable catalytic cracking product sulfur reduction catalyst according to claim 13 which is formulated with a matrix component as a fluid cracking catalyst additive.

21. A fluidizable catalytic cracking product sulfur reduction catalyst according to claim 13 which is formulated as an integrated fluidizable catalytic cracking/product sulfur reduction catalyst for cracking a heavy hydrocarbon feed to produce liquid cracking products including gasoline and reducing the sulfur content of the catalytically cracked gasoline fraction during the catalytic cracking process, which comprises fluidizable particles having a size ranging from about 20 to about 100 microns of a hydrocarbon cracking component which comprises a zeolitic molecular sieve which contains located within the pore structure of the zeolite (i) a first metal component which comprises at least one of at least one metal of Period 34, Groups 5, 8, 9 or 12 of the Periodic Table in an oxidation state greater than zero and (ii) a second metal component which comprises at least one rare earth.

22. An integrated fluidizable catalytic cracking/product sulfur reduction catalyst according to claim 21 which contains from 0.1 to 5 weight percent, based on the weight of the zeolite, of vanadium as the first metal component.

23. An integrated fluidizable catalytic cracking product sulfur reduction catalyst according to claim 21 in which the second metal component comprises a combination of

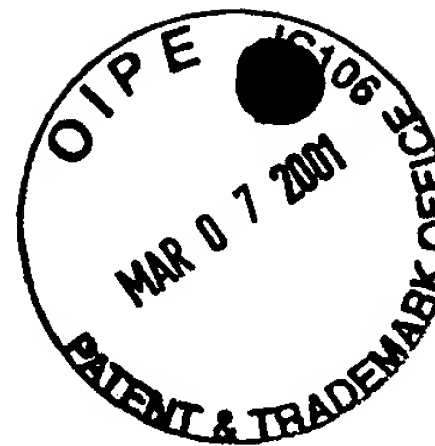
cerium and at least one other rare earth in an amount from 1 to 5 weight percent of the catalyst.

24. An integrated fluidizable catalytic cracking product sulfur reduction catalyst according to claim 21 in which the zeolitic molecular sieve comprises zeolite USY having a UCS of from 2.420 to 2.455 nm and a bulk silica:alumina ratio of at least 5.0.

25. A fluidizable catalytic cracking product sulfur reduction catalyst composition according to claim 24 in which the porous molecular sieve component comprises zeolite USY having a UCS of from 2.420 to 2.435 nm and a bulk silica:alumina ratio of at least 5.0.



Because of the concern for excessive coke and hydrogen make during the cracking process, the metals for incorporation into the additives should not exhibit hydrogenation activity to a marked degree. For this reason, the noble metals such as platinum and palladium which possess strong hydrogenation-dehydrogenation functionality are not desirable. Base metals and combinations of base metals with strong hydrogenation functionality such as nickel, molybdenum, nickel-tungsten, cobalt-molybdenum and nickel-molybdenum are not desirable for the same reason. The preferred base metals are the metals of Period 34, Groups 5, 8, 9, 12, (IUPAC classification, previously Groups 2B, 5B and 8B) of the Periodic Table. Vanadium, zinc, iron, cobalt, and gallium are effective with vanadium being the preferred metal component. It is surprising that vanadium can be used in this way in an FCC catalyst composition since vanadium is normally thought to have a very serious effect on zeolite cracking catalysts and much effort has been expended in developing vanadium suppressers. See, for example, Wormsbecher et al, *Vanadium Poisoning of Cracking Catalysts: Mechanism of Poisoning and Design of Vanadium Tolerant Catalyst System*, J. Catalysis 100, 130-137 (1986). It is believed that the location of the vanadium inside the pore structure of the sieve immobilizes the vanadium and prevents it from becoming vanadic acid species which can combine deleteriously with the sieve component; in any event, the present zeolite-based sulfur reduction catalysts containing vanadium as the metal component have undergone repeated cycling between reductive and oxidative/steaming conditions representative of the FCC cycle while retaining the characteristic zeolite structure, indicating a different environment for the metal.



## Abstract

The sulfur content of liquid cracking products, especially the cracked gasoline, of the catalytic cracking process is reduced by the use of a sulfur reduction catalyst composition comprising a porous molecular sieve which contains a metal in an oxidation state above zero within the interior of the pore structure of the sieve as well as a rare earth component which enhances the cracking activity of the cracking catalyst. The molecular sieve is normally a faujasite such as USY. The primary sulfur reduction component is normally a metal of Period 34 of the Periodic Table, preferably vanadium. The rare earth component preferably includes cerium which enhances the sulfur reduction activity of the catalyst. The sulfur reduction catalyst may be used in the form of a separate particle additive or as a component of an integrated cracking/sulfur reduction catalyst.

Periodic Table of the Elements

Period	Group Ia	Group IIa	Group IIIa	Group IVa	Group Va	Group VIa	Group VIIa	Group VIII			Group Ib	Group IIb	Group IIIb	Group IVb	Group Vb	Group VIb	Group VIIb	Group O
1 1s	1 H																1 H	2 He
2 2s2p	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3 3s3p	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 4s3d 4p	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 5s4d 5p	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6 6s (4f) 5d 6p	55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7 7s (5f) 6d	87 Fr	88 Ra	89** Ac															



* Lanthanide series 4f	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinide series 5f	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

From Cotton & Wilkinson, "Advanced Inorganic Chemistry"  
1980 by John Wiley & Sons

- Aluminum
- Antimony
- Argon
- Arsenic
- Barium
- Beryllium
- Bismuth
- Boron
- Bromine
- Cadmium
- Calcium
- Carbon
- Cerium
- Cesium
- Chlorine
- Chromium
- C salt
- Copper
- Dysprosium
- Erbium
- Europium
- Fluorine
- Gadolinium
- Gallium
- Germanium
- Gold
- Hafnium
- Helium
- Holmium

- \* Elements in
- \* Variation in
- \* Variations p
- \* Most comm
- \* A coulomet



Periodic Table of the Elements  
and ground-state electronic configurations  
(see inside back-cover for Table of Atomic Weights)

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1s <sup>1</sup>	He 1s <sup>2</sup>																
2	Li [He]2s <sup>1</sup>	Be [He]2s <sup>2</sup>																Ne 2s <sup>2</sup> 2p <sup>6</sup>
3	Na [Ne]3s <sup>1</sup>	Mg [Ne]3s <sup>2</sup>																Ar 3s <sup>2</sup> 3p <sup>6</sup>
4	K [Ar]4s <sup>1</sup>	Ca [Ar]4s <sup>2</sup>	Sc 3d <sup>1</sup> 4s <sup>2</sup>	Ti 3d <sup>2</sup> 4s <sup>2</sup>	V 3d <sup>3</sup> 4s <sup>2</sup>	Cr 3d <sup>5</sup> 4s <sup>1</sup>	Mn 3d <sup>5</sup> 4s <sup>2</sup>	Fe 3d <sup>6</sup> 4s <sup>2</sup>	Co 3d <sup>7</sup> 4s <sup>2</sup>	Ni 3d <sup>8</sup> 4s <sup>2</sup>	Cu 3d <sup>10</sup> 4s <sup>1</sup>	Zn 3d <sup>10</sup> 4s <sup>2</sup>	Ga 4s <sup>2</sup> 4p <sup>1</sup>	Ge 4s <sup>2</sup> 4p <sup>2</sup>	As 4s <sup>2</sup> 4p <sup>3</sup>	Se 4s <sup>2</sup> 4p <sup>4</sup>	Br 4s <sup>2</sup> 4p <sup>5</sup>	Kr 4s <sup>2</sup> 4p <sup>6</sup>
5	Rb [Kr]5s <sup>1</sup>	Sr [Kr]5s <sup>2</sup>	Y 4d <sup>1</sup> 5s <sup>2</sup>	Zr 4d <sup>2</sup> 5s <sup>2</sup>	Nb 4d <sup>4</sup> 5s <sup>1</sup>	Mo 4d <sup>5</sup> 5s <sup>1</sup>	Tc 4d <sup>5</sup> 5s <sup>2</sup>	Ru 4d <sup>7</sup> 5s <sup>1</sup>	Rh 4d <sup>8</sup> 5s <sup>1</sup>	Pd 4d <sup>10</sup> 5s <sup>0</sup>	Ag 4d <sup>10</sup> 5s <sup>1</sup>	Cd 4d <sup>10</sup> 5s <sup>2</sup>	In 5s <sup>2</sup> 5p <sup>1</sup>	Sn 5s <sup>2</sup> 5p <sup>2</sup>	Sb 5s <sup>2</sup> 5p <sup>3</sup>	Te 5s <sup>2</sup> 5p <sup>4</sup>	I 5s <sup>2</sup> 5p <sup>5</sup>	Xe 5s <sup>2</sup> 5p <sup>6</sup>
6	Cs [Xe]6s <sup>1</sup>	Ba [Xe]6s <sup>2</sup>	La 5d <sup>1</sup> 6s <sup>2</sup>	Hf 5d <sup>2</sup> 6s <sup>2</sup>	Ta 5d <sup>3</sup> 6s <sup>2</sup>	W 5d <sup>4</sup> 6s <sup>2</sup>	Re 5d <sup>5</sup> 6s <sup>2</sup>	Os 5d <sup>6</sup> 6s <sup>2</sup>	Ir 5d <sup>7</sup> 6s <sup>2</sup>	Pt 5d <sup>9</sup> 6s <sup>1</sup>	Au 5d <sup>10</sup> 6s <sup>1</sup>	Hg 5d <sup>10</sup> 6s <sup>2</sup>	Tl 6s <sup>2</sup> 6p <sup>1</sup>	Pb 6s <sup>2</sup> 6p <sup>2</sup>	Bi 6s <sup>2</sup> 6p <sup>3</sup>	Po 6s <sup>2</sup> 6p <sup>4</sup>	At 6s <sup>2</sup> 6p <sup>5</sup>	Rn 6s <sup>2</sup> 6p <sup>6</sup>
7	Fr [Rn]7s <sup>1</sup>	Ra [Rn]7s <sup>2</sup>	Ac 6d <sup>1</sup> 7s <sup>2</sup>	Unq	Unp	Unh	Uns											

III B	IV B	V B	VI B	VII B	0
B 2s <sup>2</sup> 2p <sup>1</sup>	C 2s <sup>2</sup> 2p <sup>2</sup>	N 2s <sup>2</sup> 2p <sup>3</sup>	O 2s <sup>2</sup> 2p <sup>4</sup>	F 2s <sup>2</sup> 2p <sup>5</sup>	Ne 2s <sup>2</sup> 2p <sup>6</sup>
13	14	15	16	17	18
Al 3s <sup>2</sup> 3p <sup>1</sup>	Si 3s <sup>2</sup> 3p <sup>2</sup>	P 3s <sup>2</sup> 3p <sup>3</sup>	S 3s <sup>2</sup> 3p <sup>4</sup>	Cl 3s <sup>2</sup> 3p <sup>5</sup>	Ar 3s <sup>2</sup> 3p <sup>6</sup>
31	32	33	34	35	36
Ga 4s <sup>2</sup> 4p <sup>1</sup>	Ge 4s <sup>2</sup> 4p <sup>2</sup>	As 4s <sup>2</sup> 4p <sup>3</sup>	Se 4s <sup>2</sup> 4p <sup>4</sup>	Br 4s <sup>2</sup> 4p <sup>5</sup>	Kr 4s <sup>2</sup> 4p <sup>6</sup>
49	50	51	52	53	54
In 5s <sup>2</sup> 5p <sup>1</sup>	Sn 5s <sup>2</sup> 5p <sup>2</sup>	Sb 5s <sup>2</sup> 5p <sup>3</sup>	Te 5s <sup>2</sup> 5p <sup>4</sup>	I 5s <sup>2</sup> 5p <sup>5</sup>	Xe 5s <sup>2</sup> 5p <sup>6</sup>
81	82	83	84	85	86
Tl 6s <sup>2</sup> 6p <sup>1</sup>	Pb 6s <sup>2</sup> 6p <sup>2</sup>	Bi 6s <sup>2</sup> 6p <sup>3</sup>	Po 6s <sup>2</sup> 6p <sup>4</sup>	At 6s <sup>2</sup> 6p <sup>5</sup>	Rn 6s <sup>2</sup> 6p <sup>6</sup>

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce 4f <sup>1</sup> 5d <sup>1</sup> 6s <sup>2</sup>	Pr 4f <sup>3</sup> 6s <sup>2</sup>	Nd 4f <sup>4</sup> 6s <sup>2</sup>	Pm 4f <sup>5</sup> 6s <sup>2</sup>	Sm 4f <sup>6</sup> 6s <sup>2</sup>	Eu 4f <sup>7</sup> 6s <sup>2</sup>	Gd 4f <sup>7</sup> 5d <sup>1</sup> 6s <sup>2</sup>	Th 6d <sup>2</sup> 7s <sup>2</sup>	Dy 4f <sup>9</sup> 6s <sup>2</sup>	Ho 4f <sup>10</sup> 6s <sup>2</sup>	Er 4f <sup>11</sup> 6s <sup>2</sup>	Tm 4f <sup>12</sup> 6s <sup>2</sup>	Yb 4f <sup>13</sup> 6s <sup>2</sup>	Lu 4f <sup>14</sup> 5d <sup>1</sup> 6s <sup>2</sup>
† 90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th 6d <sup>2</sup> 7s <sup>2</sup>	Pa 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	U 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	Np 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	Pu 5f <sup>6</sup> 7s <sup>2</sup>	Am 5f <sup>7</sup> 7s <sup>2</sup>	Cm 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	Bk 5f <sup>9</sup> 6d <sup>1</sup> 7s <sup>2</sup>	Cf 5f <sup>10</sup> 7s <sup>2</sup>	Es 5f <sup>11</sup> 7s <sup>2</sup>	Fm 5f <sup>12</sup> 7s <sup>2</sup>	Md 5f <sup>13</sup> 7s <sup>2</sup>	No 5f <sup>14</sup> 7s <sup>2</sup>	Lr 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>

\*\*† The ground-state configurations for some lanthanide and actinide elements are uncertain

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# Fluid Catalytic Cracking with Zeolite Catalysts

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dispersion), are heated at a given temperature for a time period specified to give maximum purity of the desired structure. Approximate conditions for the preparation of synthetic faujasite X are shown in Fig. 13 [15, 16, 181]. As initially crystallized, most zeolites contain sodium cations and are in the form of finely divided particles, on the order of 1 to 7  $\mu\text{m}$  [13, 101, 156, 185]. Excellent overviews of the complex area of zeolite synthesis have been published by Breck [183] and Flanigen [184].

In the next phase the preponderance of sodium may be removed by cation exchange with a medium containing rare-earth cations, or rare-earth cations plus hydrogen ion, or a cation such as ammonium ion capable of conversion to hydrogen ion [13, 17, 18, 127, 156-161]. Inexpensive rare-earth sources (as monazite or bastnasite sands), generally as the chloride salts, are utilized [13, 156-161, 181]; these are rich in cerium, lanthanum, neodymium, and praseodymium, with lesser amounts of samarium, gadolinium, etc. [181]. Comprehensive reviews on zeolitic ion exchange have been published by Sherry [186, 187].

Finally, a siliceous inorganic oxide-type sol or gel (ultimately the matrix) is produced by methods well known in the art [188] (concisely described in a review by Oblad [13]), into which the micron-sized zeolite powder is uniformly dispersed [156, 161], producing a mechanically stable, rugged, microspheroidal composite fluid catalyst after spray drying. Current commercial manufacturing practices vary widely, of course [13].

### C. Some Key Structural Features of Zeolites

The structure of zeolites (particularly rare-earth exchanged synthetic faujasites) has been discussed intensively in the literature in relation to their role in catalytic cracking [13, 17, 18, 62, 65, 76, 101, 106, 127, 131, 181, 189, 190]. Particularly relevant are overviews by Ciapetta [191], Meier and Olson [192], Oblad [13], Rabo and Poutsma [193], Smith [194], Turkevich and Ono [195], Venuto and Landis [196], and Weisz [197]. Salient features are summarized below.

Zeolites may be viewed as crystalline, inorganic polymers comprising an anionic lattice of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra linked by shared oxygen (Fig. 14). A cubo-octahedron or sodalite cage (Fig. 15A) (24 Al, Si ions, 36 oxygen anions, 8 hexagonal, and 6 square faces) represents the simplest structural building block. When sodalite units are joined in tetrahedral mode (Fig. 16B) (by bridging oxygens across the hexagonal faces), a rigid, three-dimensional reticulum—the faujasite structure (Fig. 16A)—is generated, which upon dehydration